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Description

It is standard practice to thicken aqueous compositions by including in the water a synthetic or naturally occurring, or modified naturally occurring, polymeric material that will dissolve or swell in the water. For instance for very many years it has been well known to thicken printing pastes by dissolving into them natural or modified natural materials such as sodium alginate, guar gum, hydroxy ethyl guar derivatives and starch ethers. More recently various synthetic polymers have tended to replace the natural or modified natural polymers. Generally these synthetic polymers are supplied to the user in the form of a finely divided solid which, upon incorporation into the desired aqueous medium, swells to form a micro-gel latex that serves as a thickener for the aqueous medium. Typical powdered polymers are cross-linked polymers of acrylic acid optionally with lower alkyl vinyl ether, cross-linked copolymers of maleic anhydride with alkyl vinyl ether and cross-linked copolymers of maleic anhydride with ethylene.

Although these synthetic polymers are often preferred as thickeners, for instance because of their more consistent thickening properties and because of their greater thickening efficiency than the natural polymers, their use involves many disadvantages, especially when they are used for thickening printing pastes. They have a very low bulk density making transport difficult and costly, they cause dust problems due to their content of very fine particles and they can block or wear printing screens due to their content of larger particles, and the rheology they impart to printing pastes is sometimes unsatisfactory such that it is necessary to add other polymers to impart suitable viscoelasticity to the printing pastes.

In US Patents 4,059,552 and 4,172,066 it is proposed to thicken an aqueous medium by the use of microbeads of cross-linked water insoluble, water swellable polymer. These microbeads are made by reverse phase emulsion polymerisation of appropriate monomers including cross-linking agent followed by separation of the resultant polymer particles from the oil medium in which the polymerisation was conducted.

In GB 2,007,238A it is proposed to use a blend of a water soluble polymer and a water swellable cross-linked synthetic polymer and a water swellable cross-linked synthetic polymer which, in the examples, is a cross-linked copolymer of acrylamide and 2-acrylamido-2-methyl propane sulphonic acid (AMPS) but which can, according to the description, be replaced by acrylic acid or methacrylic acid and which is made by reverse phase polymerisation. The use of copolymers of AMPS and acrylamide in printing pastes containing electrolyte is also described in GB 2,017,159A.

It is well known that it is generally preferred for a printing paste to have a pH of around 9 and at this pH any acid groups in the polymer will be in the form of a salt. Normally the polymer is made by polymerising the acrylic acid or other unsaturated acid in the form of a salt, i.e. at a high pH. For instance in the examples of US Patent 4,059,552 and GB 2,007,238A each of the polymerisations conducted on an acidic monomer is conducted in the presence of sufficient sodium hydroxide to convert all the acid groups to salt form. It is also known to polymerise monomers such as acrylic acid whilst wholly in the free acid form.

In each of these disclosures the polymer particles always have a size which is, when dry, very small, below 10µm. Processes of making much larger sized beads of cross linked swellable polymers are also known, such beads then being useful as absorbents. It is described in GB 2,088,392 that one known process gives an average particle diameter of 40 to 50µm and the purpose of the process in GB 2,088,392 is to make larger particle sizes, and in particular the described process gives particles having a size of 100 to 3,000µm. For instance in example 1 an aqueous solution of 15g acrylic acid and 6.7g sodium hydroxide was subjected to reverse phase polymerisation to give particles having an average diameter of 300µm. Clearly such a process, aimed at achieving large particle sizes, is of no relevance to the problem of how to produce very small particle size, below 10µm, dispersions having improved thickening properties when used in the form of dispersions.

It would be desirable to be able to produce improved thickeners that give improved thickening effects in, for instance, printing pastes and to provide thickeners in convenient, and readily usable, form.

In one aspect of the invention we have surprisingly found that it is possible to vary the thickening effect of such polymers containing acid groups by adjusting the proportion of acid groups to salt groups that are present during the polymerisation and, in particular, that by having certain proportions of such groups it is possible to obtain a greatly improved thickening effect compared to that obtained when the polymerisation is conducted with all the acid groups in free acid form or all the acid groups in salt form.

In this aspect of the invention, there is provided the use of a polymer dispersion as a thickener for an aqueous composition, in which the polymer dispersion is a dispersion in water immiscible liquid of particles of a water insoluble, water swellable or swollen polymer having a dry particle size of below 10µm and that has been made by reverse phase polymerisation of a water soluble blend of copolymerisable monomers that comprises (a) at least one ethylenically unsaturated acid having free acid groups, (b) at least one

ethylenically unsaturated acid having salt groups selected from ammonium, amine and alkali metal salt groups, and (c) at least one ethylenically unsaturated cross-linking agent and the molar proportions of the said free acid groups to the said salt groups during the polymerisation are from 80:20 to 10:90. Although bifunctional acids can be used it is generally preferred that each of the acids (a) and (b) should be monocarboxylic or monosulphonic acids, generally monocarboxylic acids, in which event the molar proportions of the monomer in free acid form to the monomer in salt form must be 80:20 to 10:90.

Typical acids that can be used include vinyl sulphonic acid, sulphopropyl acrylate or methacrylate, itaconic acid, crotonic acid, maleic acid and fumaric acid but the preferred acids are AMPS or, especially, acrylic or methacrylic acid, acrylic acid generally being the most suitable monomer. The monomers (a) and (b) may be provided by partial neutralisation of monomer having free acid groups or may be made by blending monomer having free acid groups with a monomer, which may be the same or different as the free acid monomer, having salt groups. A blend of two or more monomers having free acid groups may be used and/or a blend of two or more monomers having salt groups may be used.

The salt groups are preferably ammonium groups but they may be of an alkali metal, generally sodium but optionally potassium or any other suitable alkali metal, or of an amine, generally an aliphatic amine. Suitable amines are primary and secondary aliphatic amines, generally primary and secondary alkylamines or alkanolamines, for instance methylamine, ethylamine, monoethanolamine or diethanolamine. The free acid form of the monomer may be converted to the salt form by adding a suitable base, such as a hydroxide, that will provide the desired ammonium, amine or alkali metal ion in conventional manner.

The ethylenically unsaturated cross-linking agent may be any material that is suitable for cross-linking acrylic monomers, and many such materials are known and include methylene bisacrylamide, allyl methacrylate, diallyl phthalate and glycol diacrylates. Methylene bisacrylamide is generally preferred.

The optimum thickening effect is obtained when the said molar ratio is between 70:30 and 20:80, most preferably between 65:35 and 30:70. When the acid for both (a) and (b) is acrylic acid the specified proportions indicate that the pH during the polymerisation should be from 3.7 to 5.5 and preferably from 4.3 to 5.2. With other acids the pH range may be different depending upon the strength of the acid.

The blend may include unsaturated monomers (d) additional to the types (a), (b) and (c) and that can be copolymerised with them. Usually these additional monomers are ethylenically unsaturated. Typical addition monomers include hydroxy ethyl acrylate or methacrylate, N-vinyl-N-methylacetamide and acrylamide. The amount may be up to 60 mole %. If additional monomer (d) is to be included then acrylamide is generally the preferred additional monomer.

The amount of cross-linking agent is generally from 2×10^{-3} to 150×10^{-3} mole percent, preferably 10×10^{-3} to 40×10^{-3} mole percent based on moles of polymerisable monomers. For instance when the monomers are free acrylic acid and acrylic acid salt and the cross-linking agent is methylene bisacrylamide the amount is preferably from 42 to 3,200 ppm, most preferably 200 to 850 ppm by weight on weight of polymer.

The properties of the polymer can be varied by appropriate choice of amount of cross-linking agent and the average molecular weight of the copolymer and the molecular weight distribution of the copolymer. A meaningful way of defining the molecular weight of the copolymer is to define the intrinsic viscosity of the polymer obtained using the identical polymerisation conditions but in the absence of cross-linking agent. In the invention the intrinsic viscosity under these circumstances measured at 25°C in 1 M sodium chloride solution buffered to pH 7.0 is preferably from 4 to 20 dl gm^{-1} , most preferably 8 to 10 or 14. The polymerisation should therefore be conducted using initiator concentrations and/or chain transfer agents in known manner to achieve these levels of intrinsic viscosity.

The polymerisation is conducted as a reverse phase polymerisation, for instance as is described generally in US 4,059,552. Thus an aqueous solution of the monomer blend is dispersed in a water-immiscible liquid and is polymerised to form a dispersion of polymer particles, swollen by water, in the water-immiscible liquid. The water-immiscible liquid may comprise mineral oil, kerosene, dibutyl phthalate or vegetable oil and is generally a hydrocarbon or halogenated hydrocarbon. It will generally include a suspending agent, preferably a polymeric suspension polymerisation stabiliser, most preferably one formed from hydrophilic and hydrophobic monomers, for instance as described in EP 1,482,515, EP 0,126,528 or US 4,339,371. It may also contain a water-in-oil emulsifier of HLB 3 to 8, generally below 7. The amount of emulsifier is generally very low and, if present at all, serves solely to facilitate reducing the particle size of the aqueous monomer droplets. Polymerisation is therefore preferably a reverse phase suspension polymerisation, polymerisation occurring primarily within the monomer droplets generally using a water-soluble initiator. The aqueous monomer solution is homogenised into the water-immiscible liquid to form the aqueous monomer droplets, the suspension may then be deoxygenated and polymerisation initiated in conventional manner, for instance by adding a suitable radical-producing initiator. The dry size of the

resultant polymer particles is preferably 0.2 to 3 μm .

The product of the polymerisation is a dispersion in water-immiscible liquid of aqueous polymer particles. It is often preferred that the product should be dehydrated. For instance the continuous phase may include a volatile hydrocarbon or chlorinated hydrocarbon and the product may then be subjected to azeotropic distillation to reduce the water content to below 25% by weight polymer, generally below the ambient moisture content of the polymer particles when exposed to the atmosphere.

When acrylamide is copolymerised with acrylic acid, or a salt thereof or any other acrylic or other copolymerisable monomers, it might be expected that the effect of the acrylamide on the final polymer properties could vary directly or indirectly in proportion to the amount of acrylamide in the blend of monomers.

We have surprisingly found that the effect is not proportional but that very low and medium amounts give a valuable improvement in thickening properties whilst low and high amounts are less desirable. In particular we find that the amount of acrylamide should be from 0 to 3% or from 13 to 45% with best results being achieved either with 0% or with 15 to 45% acrylamide (the percentages being mole percent in the copolymer).

According to a second aspect of the invention, there is provided the use of a polymer dispersion as a thickener for an aqueous composition in which the polymer dispersion is a dispersion in water immiscible liquid of water insoluble, water swellable or water swollen polymer particles having a dry size of below 10 μm and that has been made by reverse phase polymerisation of a water soluble blend of copolymerisable monomers that comprise at least one ethylenically unsaturated monomer, generally selected from the monomers (a), (b) and (d) discussed above, at least one ethylenically unsaturated cross-linking agent, generally selected from the monomers discussed above for (c), and 13 to 45% (molar) acrylamide.

Preferably the polymer will have been made by reverse phase polymerisation and preferably it will have been made using a blend of monomers (a) and (b) as discussed above, but this aspect of the invention is also of value when the polymerisation is, for instance, conducted in the absence of monomer (a).

If acrylamide is present, the preferred amount is generally from 20 to 40%, most preferably 25 to 35%. All these values are indicated on the basis of thickening efficiency. When the copolymer is being used for thickening a fabric printing paste an additional desirable property is that it should be possible to wash the thickener out of the fabric. High amounts, for instance above 40 mole percent, acrylamide make it difficult to wash the fabric thoroughly, resulting in a stiffer hand and poor drape qualities.

A particular advantage with the specified very low or medium amounts of acrylamide arises when the polymer is initially provided as a dispersion in water-immiscible liquid of aqueous polymer particles and this dispersion is then dehydrated, for instance by azeotropic distillation as discussed above. We have surprisingly found that thickener dispersions of this general type that have dehydrated and in which the polymer contains no acrylamide or is formed from the specified very low or medium amounts of acrylamide have much better thickening properties, after the azeotropic distillation, than the corresponding dispersions containing polymer formed from other amounts of acrylamide.

When the dehydrated dispersions used in the invention are made by azeotropic distillation of an aqueous dispersion, it is generally necessary to add ammonia or volatile amine after distillation since it is preferred for the substantially all the acid groups in the dispersions used in the invention to be neutralised with ammonia or volatile amine. These compositions have the advantage that they can be supplied to the print paste manufacturer and can be used to form an alkaline print paste containing a volatile base without the need for the manufacturer to add ammonia or volatile amine.

The compositions are used for thickening an aqueous medium without prior separation of the polymer particles from the water-immiscible liquid. Thus the dispersion of particles in the water-immiscible liquid is added to an aqueous medium in order to produce microgel latex thickening of that medium. To facilitate emulsification of the dispersion in the aqueous medium an emulsifier, generally an oil-in-water emulsifier, may be added to facilitate emulsifying the oily continuous phase in water and thereby allowing the dispersed polymer particles to be wetted by water and to swell to form the microgel latex. The amount of polymer in the aqueous medium is generally from 0.05 to 5%, most preferably 0.1 to 1% by weight.

The pH of the aqueous medium should be such that substantially all the acid groups are ionised and in practice this generally means that the pH should be at least 8. The viscosity drops markedly when the pH falls below the level indicating complete ionisation, and also, at desirably low pH values, the dispersion may gel on storage. If the pH is too high the viscosity may drop due to an electrolytic effect and generally the pH should be between 7 and 10 with best results being achieved around 8.5 to 9.5. Amine, ammonium compound or alkali metal compound may be added to the dispersion of polymer particles in water-immiscible liquid in order to raise the pH of the eventual aqueous medium or such compound may be added to the aqueous medium. Generally the compound used for this purpose is sodium hydroxide.

ammonia or an amine.

The thickened aqueous medium can be used for a wide variety of purposes but most preferably serves as the aqueous medium of a printing paste that additionally comprises a pigment or dye. The invention includes not only the described method of polymerisation, the compositions resulting from this and thickened aqueous media, including print paste, containing the resultant polymer as thickening agent but also includes methods in which a substrate is printed with an aqueous print paste thickened by the described polymer and comprising a pigment or dye. The print paste may be formulated in conventional manner, except for the use of the specified polymer as the thickening agent, and thus may include conventional additives such as inorganic salts, urea, coacervating agents such as coconut diethanolamide, softening agents such as dibutyl phthalate, dioctyl phthalate and fatty glyceride esters, lubricants such as silicone oils, pigment dispersants such as low molecular weight polyacrylic acid, wetting agents such as diethyhexylsulphosuccinate and emulsifiers such as ethoxylated nonyl phenol and ethoxylated fatty alcohols.

Aqueous pastes for pigment printing will generally include also a synthetic binder, most preferably an alkyl (usually methyl, ethyl or butyl) acrylate binder cross-linked with, for instance, methylol acrylamide, the binder optionally also being formed from one or more hardening monomers such as styrene, acrylonitrile or methyl methacrylate. Other suitable binders include butadiene copolymers.

The colourant in the print paste may be one of a wide variety of pigments and dyes, that may be water soluble or water dispersible, for instance pigment, acid dyes, disperse dyes and reactive dyes. For many printing pastes the salt forming cation is preferably volatile, for instance ammonia, in order that the cation evaporates during drying of the paste. However in others, for instance when the colourant is a reactive dye, the cation should be sodium in order that the dye will react with the cellulosic substrate under alkaline conditions.

The defined polymers have proved to be valuable thickening agents in a wide range of printing processes, for instance by engraved roller machines, hand or machine flat bed screen printing or rotary screen printing, on a wide range of substrates, for instance textiles, floor coverings and paper. The precise details of the paste will be formulated in known manner, according to the particular printing method and substrate being used. A surprising advantage of the described polymers is that pastes thickened by them give a very high colour yield and definition, and other desirable characteristics. A particularly striking advantage of the first aspect of the invention is that as a result of the increased thickening effect obtainable as a result of the blend of monomers (a) and (b) during the polymerisation the amount of thickener required to achieve any particular viscosity can be greatly reduced compared to the amount required when the polymerisation is conducted using monomer (a) alone or monomer (b) alone. For instance in order to obtain a viscosity of 25 Pa.s (250 poise) it is possible by the invention, to reduce the required amount of polymer by 20 to 30% or more.

The following are examples of the invention:

EXAMPLE 1

An aqueous monomer solution was formed containing 0.4875 mole % of monomers based on weight of aqueous phase, 0.24×10^{-4} mole % penta sodium diethylenetriamine pentacetate based on weight of aqueous phase, 26.6×10^{-3} mole % of cross-linking agent (methylene bisacrylamide) based on moles of monomers and 8.6×10^{-3} mole % of azobisisobutyronitrile hydrochloride based on moles of monomers. The monomers contained 20 mole % acrylamide and 80 mole % of one of various mixtures of acrylic acid and ammonium acrylate in molar ratios between 100:0 and 0:100.

A non-aqueous continuous phase was a mixture of 44% by weight mineral oil and 56% by weight volatile hydrocarbon fraction of boiling range 154-168°C containing as dispersion stabiliser a mixture of 46% by weight of a 6 to 1 molar copolymer of octo-stearyl methacrylate to trimethyl beta-methacryloxyethylammonium methosulphate and 54% by weight of sorbitan monooleate. The total concentration of dispersion stabiliser used was 1.9×10^{-2} mole % on weight of aqueous phase based on the molecular weight per hydrophobic group in the surfactants. The weight ratio of oil phase to aqueous phase was 0.8833.

The aqueous monomer phase was mechanically homogenised into the oil phase and the resulting dispersion was then deoxygenated in a stirred polymerisation reactor and polymerisation initiated by 48.1×10^{-3} mole % of sulphur dioxide and 0.68×10^{-3} mole % per minute of tertiary butyl hydroperoxide based on moles of monomer.

The resultant polymerised dispersion was distilled at a pressure of 2660 Pa (20 Torr) and rendered water dispersible by adding a 7 mole ethoxylate of nonyl phenol equivalent to 5% by weight on weight of a

dispersion containing 45% by weight of copolymer calculated as the free acid.

A sample of the dispersion was diluted in water containing sodium chloride and titrated potentiometrically to determine the polymer content. The dispersion was then diluted as necessary with hydrocarbon oil to exactly 45.0% w/wt polymer content.

Each of the dispersions was made up into a pigmented print paste at various concentrations by blending 4 parts by weight pigment (Imperon Blue KRR) 8 parts by weight binder latex (based on ethyl acrylate cross-linked with methylol acrylamide), sufficient 0.880 ammonia solution to give a pH in the paste of 9.0, the polymer dispersion, and sufficient water to give 100 parts by weight.

The pigment print paste viscosities were measured using a Brookfield Viscometer Type RVT at speed 10 rpm at 20° C. The results are shown in Table 1. Viscosities are given in Pa.s and the % polymer is quoted as a weight % in the print paste as the fully neutralised ammonium salt when present in the ammoniacal print paste.

TABLE 1

Polymer Dispersion	Molar Ratio of acrylic acid to ammonium acrylate	Monomer Solution pH	Brookfield Viscosity			% Polymer required to give 25 Pa.s
			1.1% w/w polymer	1.0% w/w polymer	0.9% w/w polymer	
1A	100:0	2.20	75	45	24	1.449
1B	80:20	3.70	295	220	155	1.033
1C	70:30	4.20	325	250	190	1.000
1D	60:40	4.50	445	325	223	0.925
1E	50:50	4.70	435	325	230	0.918
1F	40:60	5.00	425	310	214	0.934
1G	30:70	5.20	395	305	226	0.936
1H	20:80	5.30	365	275	183	0.973
1I	15:85	5.35	355	255	164	0.991
1J	10:90	5.45	350	255	160	0.996
1K	5:95	5.75	215	160	117	1.147
1L	0:100	7.15	185	140	106	1.208

It can be seen from these results that polymers prepared with either acrylic acid alone or ammonium acrylate alone are very much less efficient as print paste thickeners than polymers prepared with both acrylic acid and ammonium acrylate in molar ratios within the scope of the invention.

EXAMPLE 2

The process of example 1 was repeated except that the molar ratio of acrylic acid to ammonium acrylate was 40:60 and the mole % acrylamide was varied from 0 to 65%. A pigmented print paste was prepared from each copolymer using 4 parts Imperon Blue KRR, 8 parts of the binder of example 1, 0.5 parts of 0.880 ammonia, 85.5 parts water and 2 parts of 50% active by weight polymer dispersion (calculated as fully neutralised polymer). The paste viscosity of each paste was recorded. The results are

shown in Table 2.

TABLE 2

Polymer	Mole % ACM in copolymer	Paste Viscosity (Pa.s)
2A	0	318
2B	2.96	290
2C	5.90	240
2D	11.72	275
2E	17.40	312
2F	28.47	323
2G	53.90	240
2H	64.95	164

This demonstrates the disadvantage of using between about 3 and 15% or above about 45% acrylamide. When the pastes were printed onto polyester/cotton cloth it was found that polymer 2A gave slightly inferior dry cleaning fastness.

Typically, each paste was printed on 50/50 polyester/cotton cloth with a 156T screen having a number of patterned and blotch printing areas using a Johannes Zimmer laboratory printing machine, type MDF-240 with a 9mm bar, magnet pressure 3 and magnet speed 5. The wet prints were allowed to stand for 5 minutes before drying and curing in a hot air draught at 150 °C for 4 minutes.

EXAMPLE 3

A monomer blend of 10 mole % acrylic acid, 90 mole % ammonium acrylate and zero % acrylamide, was polymerised by the same general technique as in Example 1 except that the resulting polymer dispersion was not distilled, and ammonia was added to the aqueous dispersion in an amount sufficient to neutralise all the acrylic acid groups and to give a dispersion containing 26% by weight ammonium polyacrylate. A pigmented print paste was prepared as in Example 1 using 4 parts Imperon Blue KRR, 8 parts binder latex, 3.85 parts of polymer dispersion and 84.15 parts water.

The paste was of pH 8.2 and had a Brookfield Viscosity at 10 rpm of 24 Pa.s (240 Poise.) The paste was printed onto 50/50 polyester/cotton cloth as in example 2 and the print was a bright blue of excellent definition and colour yield and was found to have good rub fastness and wash fastness.

EXAMPLE 4

A blend of 25 mole % acrylic acid and 75 mole % ammonium acrylate was polymerised by the same general technique as in Example 1 except that the dispersion stabiliser mixture was formed of 75% by weight of a 2:1 molar copolymer of ceto stearyl methacrylate to methacrylic acid and 25% by weight sorbitan monooleate and the aqueous phase contained 0.4722 mole % of monomers based on weight of aqueous phase, 0.795×10^{-4} mole % of penta sodium diethylenetriamine pentacetate based on weight of aqueous phase, 5.13×10^{-2} mole % of mono-sodium phosphate dihydrate based on weight of aqueous phase, 21.76×10^{-3} mole % of cross-linking agent (methylene-bisacrylamide) based on moles of monomers and 9.2×10^{-3} mole % of azobisisamidinopropane hydrochloride based on moles of monomers. The

dispersion obtained upon polymerisation and distillation was rendered water dispersible by adding 7.3% by weight on weight of final oil phase a phosphoric acid ester of a 5 mole ethoxylate of tridecanol and 7.3% by weight on weight of final oil phase of a 7 mole ethoxylate of nonyl phenol.

- 5 A stock thickening was prepared by blending 97% by weight water, 0.5% by weight 0.880 ammonia and 2.5% by weight of the resultant polymer dispersion (1.25% polymer solids). This clear stock thickening had a Brookfield Viscosity of 24 Pa.s (240 Poise) measured at 10 rpm with spindle 6 at 20 °C. 1% by weight of a disperse dye-stuff including a low concentration of electrolyte (Seriprint Red RLS) was blended into the stock to form a paste having a Brookfield Viscosity of 21.4 Pa.s (214 Poise) at 10 rpm spindle 6
 10 20 °C. Upon printing on polyester poplin in conventional manner excellent colour yield and definition with minimal fabric penetration was obtained.

Claims

- 15 1. Use of a polymer dispersion as a thickener for an aqueous composition, in which the polymer dispersion is a dispersion in water immiscible liquid of particles of a water insoluble, water swellable or swollen polymer having a dry particle size of below 10µm and that has been made by reverse phase polymerisation of a water soluble blend of copolymerisable monomers that comprise at least one
 20 ethylenically unsaturated acid and at least one ethylenically unsaturated cross-linking agent characterised in that the at least one ethylenically unsaturated acid comprises (a) at least one ethylenically unsaturated acid having free acid groups and (b) at least one ethylenically unsaturated acid having salt groups selected from ammonium, amine and alkali metal salts and the molar ratio of the said free acid groups to the said salt groups during the polymerisation is from 80:20 to 10:90.
- 25 2. A use according to claim 1 in which each of the acids (a) and (b) are selected from monocarboxylic and monosulphonic acids, preferably acrylic, methacrylic or 2-acrylamido-2-methylpropane sulphonic acid.
- 30 3. A use according to either preceding claim in which the blend of monomers (a) and (b) was obtained by partially neutralising at least one ethylenically unsaturated free acid with an alkali metal compound, an amine compound or an ammonium compound.
- 35 4. A use according to any preceding claim in which the monomers consist essentially of (a) a free acid selected from acrylic acid and methacrylic acid, (b) an acid selected from acrylic acid and methacrylic acid and in the form of a salt selected from ammonium, amine and alkali metal salts wherein the molar ratio of free acid:salt is from 80:20 to 10:90, (c) 15 to 40% acrylamide, and (d) at least one ethylenically unsaturated cross-linking agent.
- 40 5. A use according to any preceding claim in which the monomers comprise up to 80 mole %, based on the total monomers, of at least one ethylenically unsaturated copolymerisable monomer that does not contain acid groups in the form of free acid groups or salt groups and the said molar ratio is preferably between 65:35 and 30:70.
- 45 6. Use of a polymer dispersion as a thickener for an aqueous composition, in which the polymer dispersion is a dispersion in water immiscible liquid of water insoluble, water swellable or water swollen polymer particles having a dry size of below 10µm that has been made by reverse phase polymerisation of a water soluble blend of copolymerisable monomers that comprise at least one ethylenically unsaturated acid, at least one ethylenically unsaturated cross-linking agent and 0 to 60% molar other ethylenically unsaturated monomers characterised in that the monomers include from 13 to
 50 45% molar of acrylamide.
7. A use according to claim 4 or claim 6 in which the amount of acrylamide is 20% to 40% molar.
- 55 8. A use according to any preceding claim in which the amount of ethylenically unsaturated cross-linking agent is from 2×10^{-3} mole % to 150×10^{-3} mole % and the intrinsic viscosity of the polymer, in the absence of the cross-linking agent, is from 4 to 20 dl gm⁻¹ measured at 25 °C in 1M sodium chloride aqueous solution buffered at pH 7.

9. A use according to any preceding claim in which, after the reverse phase polymerisation process, the dispersion has been then dehydrated by azeotropic distillation to reduce the water content of the particles to below 25% by weight of polymer.
10. A use according to any preceding claim in which the reverse phase polymerisation is a reverse phase suspension polymerisation process conducted in the presence of a polymeric suspension polymerisation stabiliser.
11. A use according to any preceding claim in which the pH of the aqueous composition is such that substantially all acid groups in the polymer are neutralised with ammonia or a volatile amine.
12. A use according to any preceding claim in which the aqueous composition is a print paste additionally comprising a pigment or dye.

Revendications

1. Utilisation d'une dispersion de polymère, à titre d'épaississant pour une composition aqueuse, dans laquelle la dispersion de polymère est une dispersion, dans un liquide non miscible à l'eau, de particules d'un polymère insoluble dans l'eau, gonflable dans l'eau ou gonflé par l'eau, ayant une taille de particules sèches inférieure à 10 µm et qui a été obtenu par polymérisation avec inversion de phase d'un mélange hydrosoluble de monomères copolymérisables comprenant au moins un acide à insaturation éthylénique et au moins un agent de réticulation, à insaturation éthylénique, l'utilisation étant caractérisée en ce que l'au moins un acide à insaturation éthylénique comprend (a) au moins un acide à insaturation éthylénique ayant des groupes acide libre et (b) au moins un acide à insaturation éthylénique ayant des groupes salins choisis parmi des sels d'ammonium, d'amine et de métal alcalin, et en ce que le rapport molaire desdits groupes acide libre auxdits groupes salins se situe pendant la polymérisation entre 80:20 et 10:90.
2. Utilisation selon la revendication 1, dans laquelle chacun des acides (a) et (b) est choisi parmi des acides monocarboxyliques et monosulfoniques, de préférence l'acide acrylique, l'acide méthacrylique ou l'acide 2-acrylamido-2-méthylpropane sulfonique.
3. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle on a obtenu le mélange des monomères (a) et (b) en soumettant au moins un acide libre à insaturation éthylénique à neutralisation partielle à l'aide d'un composé de métal alcalin, d'une amine ou d'un composé d'ammonium.
4. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle les monomères consistent essentiellement en (a) un acide libre choisi parmi l'acide acrylique et l'acide méthacrylique (b) un acide choisi parmi l'acide acrylique et l'acide méthacrylique et sous forme d'un sel choisi parmi un sel d'ammonium, d'amine et de métal alcalin, le rapport molaire acide libre:sel se situant entre 80:20 et 10:90 ; (c) 15 à 40 % d'acrylamide, et (d) au moins un agent de réticulation à insaturation éthylénique.
5. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle les monomères comprennent jusqu'à 60 mol %, sur la base des monomères totaux; d'au moins un monomère copolymérisable, à insaturation éthylénique, ne contenant pas de groupes acides sous forme de groupes acide libre ou de groupes salins, et ledit rapport molaire se situe de préférence entre 65:35 et 30:70.
6. Utilisation d'une dispersion de polymère, à titre d'épaississant pour une composition aqueuse, dans laquelle la dispersion du polymère est une dispersion, dans un liquide non miscible à l'eau, de particules d'un polymère insolubles dans l'eau, gonflables par l'eau ou gonflées, ayant une taille à sec inférieure à 10 µm, particules qui ont été préparées par polymérisation avec inversion de phase d'un mélange hydrosoluble de monomères copolymérisables comprenant au moins un acide à insaturation éthylénique, au moins un agent de réticulation à insaturation éthylénique et 0 à 60 mol % d'autres monomères à insaturation éthylénique, utilisation caractérisée en ce que les monomères comprennent

de 13 à 45 mol % d'acrylamide.

7. Utilisation selon la revendication 4 ou 6, dans laquelle la proportion d'acrylamide représente 20 mol % à 40 mol %.
8. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle la quantité de l'agent de réticulation à insaturation éthylénique se situe entre 2×10^{-3} mol % et 150×10^{-3} mol %, et la viscosité intrinsèque du polymère, en l'absence de l'agent de réticulation, se situe entre 4 et 20 dl g⁻¹, quand cette viscosité est mesurée à 25 °C dans une solution aqueuse de chlorure de sodium 1M tamponnée à pH 7.
9. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle, après le procédé de polymérisation avec inversion de phase, la dispersion a été déshydratée par distillation azeotropique peut réduire à une valeur, inférieure à 25 % du poids du polymère, la teneur en eau de particules.
10. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle la polymérisation avec inversion des phases est un procédé de polymérisation en suspension avec inversion des phases, procédé conduit en présence d'un stabilisant polymère de polymérisation en suspension.
11. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le pH de la composition aqueuse est tel que la quasi-totalité des groupes acides du polymère sont neutralisés par l'ammoniaque ou par une amine volatile.
12. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle la composition aqueuse est une pâte d'impression comprenant en outre un pigment ou un colorant.

Ansprüche

1. Verwendung einer Polymerdispersion als Verdickungsmittel für eine wässrige Zusammensetzung, worin die Polymerdispersion eine Dispersion in einer mit Wasser nicht mischbaren Flüssigkeit von Teilchen eines wasserunlöslichen, in Wasser quellbaren oder gequollenen Polymers mit einer Partikelgröße von unter 10 µm im trockenen Zustand ist, und das hergestellt wurde durch Polymerisation in umgekehrter Phase einer wasserlöslichen Mischung von copolymerisierbaren Monomeren, welche mindestens eine ethylenisch ungesättigte Säure und mindestens ein ethylenisch ungesättigtes Vernetzungsmittel umfassen, dadurch gekennzeichnet, daß die mindestens eine ethylenisch ungesättigte Säure (a) mindestens eine ethylenisch ungesättigte Säure mit freien Säuregruppen und (b) mindestens eine ethylenisch ungesättigte Säure mit Salzgruppen, ausgewählt aus Ammonium-, Amin- und Alkalimetallsalzen, umfaßt, und das molare Verhältnis der freien Säuregruppen zu den Salzgruppen während der Polymerisation 80 : 20 bis 10 : 90 beträgt.
2. Verwendung nach Anspruch 1, worin jede der Säuren (a) und (b) ausgewählt sind aus Monocarbonsäuren und Monosulfonsäuren, vorzugsweise Acrylsäure, Methacrylsäure oder 2-Acrylamido-2-methylpropanesulfonsäure.
3. Verwendung nach einem der vorhergehenden Ansprüche, worin die Mischung von Monomeren (a) und (b) durch partielle Neutralisierung mindestens einer ethylenisch ungesättigten freien Säure mit einer Alkalimetallverbindung, einer Aminverbindung oder Ammoniumverbindung erhalten wurde.
4. Verwendung nach irgendeinem der vorhergehenden Ansprüche, worin die Monomeren im wesentlichen aus (a) einer freien Säure, ausgewählt aus Acrylsäure und Methacrylsäure und (b) einer aus Acrylsäure und Methacrylsäure ausgewählten Säure in Form eines Salzes ausgewählt aus Ammonium-, Amin- und Alkalimetallsalzen, worin das molare Verhältnis von freier Säure : Salz 80 : 20 bis 10 : 90 beträgt. (c) 15 bis 40% Acrylamid, und (d) mindestens einem ethylenisch ungesättigten Vernetzungsmittel bestehen.
5. Verwendung nach irgendeinem der vorhergehenden Ansprüche, worin die Monomeren bis zu 60 Mol-%, bezogen auf die Gesamtmonomeren, an mindestens einem ethylenisch ungesättigten copolymerisierbaren Monomer, welches keine Säuregruppen in Form von freien Säuregruppen oder Salzgruppen

enthält, umfassen und das molare Verhältnis vorzugweise zwischen 65 : 35 und 30 : 70 beträgt.

6. Verwendung einer Polymerdispersion als Verdickungsmittel für eine wäßrige Zusammensetzung, worin die Polymerdispersion eine Dispersion in einer mit Wasser nichtmischbaren Flüssigkeit von in Wasser unlöslichen, in Wasser quellbaren oder in Wasser gequollenen Polymerpartikeln mit einer Größe von unter 10 µm im trockenen Zustand, welche durch Polymerisation in umgekehrter Phase einer wasserlöslichen Mischung von copolymerisierbaren Monomeren, die mindestens eine ethylenisch ungesättigte Säure, mindestens ein ethylenisch ungesättigtes Vernetzungsmittel und 0 bis 60 Mol-% anderer ethylenisch ungesättigter Monomeren umfassen, hergestellt wurden, dadurch gekennzeichnet, daß die Monomeren 13 bis 45 Mol-% Acrylamid einschließen.
7. Verwendung nach Anspruch 4 oder Anspruch 6, worin die Menge an Acrylamid 20 bis 40 Mol-% beträgt.
8. Verwendung nach irgendeinem der vorhergehenden Ansprüche, worin die Menge an ethylenisch ungesättigten Vernetzungsmitteln von 2×10^{-3} Mol-% bis 150×10^{-3} Mol-% reicht, und die Grenzviskositätszahl des Polymers in Abwesenheit des Vernetzungsmittels 4 bis 20 dl g⁻¹ beträgt, gemessen bei 25 °C in wäßriger 1M Natriumchloridlösung, die bei pH 7 gepuffert ist.
9. Verwendung nach irgendeinem der vorhergehenden Ansprüche, worin nach der Polymerisation in umgekehrter Phase die Dispersion durch azeotrope Destillation entwässert wurde, um den Wassergehalt der Teilchen auf unter 25 Gew.-% des Polymers zu verringern.
10. Verwendung nach irgendeinem der vorhergehenden Ansprüche, worin die Polymerisation in umgekehrter Phase ein Suspensionspolymerisationsverfahren in umgekehrter Phase ist, welches in Gegenwart eines polymeren Suspensions-Polymerisationsstabilisators durchgeführt wird.
11. Verwendung nach irgendeinem der vorhergehenden Ansprüche, worin der pH der wäßrigen Zusammensetzung solcherart ist, daß im wesentlichen alle Säuregruppen im Polymer mit Ammoniak oder einem flüchtigen Amin neutralisiert sind.
12. Verwendung nach irgendeinem der vorhergehenden Ansprüche, worin die wäßrige Zusammensetzung eine Druckpaste ist, welche zusätzlich ein Pigment oder einen Farbstoff umfaßt.